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EVALUATION OF THREE PROTECTIVE COATINGS FOR INDOOR SILVER ARTIFACTS

Chandra L. Reedy, Richard A. Corbett, Deborah L. Long, Robert E. Tatnall, and Bradley D. Krantz

Abstract

Three coatings commonly used for protection of silver artifacts housed indoors (Agateen, Paraloid B-72, and Paraloid B-48N) were tested to rank their performance. Protocols were developed to be relevant to conservation practice, while also incorporating industry testing techniques. A variety of test specimens were used to check for effects of complex geometry and sterling versus fine silver, and to measure changes occurring on the silver beneath the coatings as well as changes of the coatings themselves. Accelerated aging included exposure to fluctuating temperature and relative humidity, and to a variety of common pollutants (hydrogen sulfide, sulfur dioxide, ozone, formaldehyde, and acetic acid). Both visual ranking and quantitative tests were used; data were analyzed for statistical significance by one-way and two-way analysis of variance. Our results show that Agateen protects silver from hydrogen sulfide, even after great environmental stress (i.e., accelerated aging), whereas the two acrylic coatings offer no protection. All three coatings begin to crack and peel slightly after accelerated aging. For the bent specimens with more complex geometry, brushing provides better protection, as otherwise the coatings tend to peel away from edges. For protection against hydrogen sulfide, spraying was sometimes more effective, perhaps because it may result in a slightly thicker and more even coating. Our findings correspond with our field observations and the reported experiences of many conservators. Conservators are sometimes reluctant to use Agateen due to problems with other cellulose nitrate lacquers and to the severe degradation any cellulose nitrate can endure if exposed to very high temperatures or to direct sunlight. However, given the preferred application and appearance qualities of Agateen, our results support its continued use for coating of silver for indoor environments.

1. Introduction

Most silver artifacts in the collections of museums and historic buildings are coated to protect against the easily-developed tarnish that detracts from the appearance of objects, obscures important details, and creates time-intensive cleaning and polishing maintenance work. The choice of coating is crucial, since coating failure can result in even more destruction to the object than occurs with no coating at all. A failed coating may require significant time for removal, cleaning, and recoating. However, the repertoire of coatings currently in use in the conservation field is rather limited. Only limited test reports of those coatings exist in the literature and the use of some is controversial, with conservators reporting conflicting experiences with their use.

Reviewing the limited number of studies of coatings for metal artifacts housed indoors, the one most frequently cited by conservators was published about 25 years ago (De Witte 1973). In this study, thirteen coatings were tested. The tests were not actually performed on silver or copper specimens, but rather on tin-plated iron. The testing protocol has been criticized because of the use of an extremely high temperature (90°C). Such an extreme temperature is not realistic for most conservation applications and, most importantly, is known to thermally decompose some of the coatings tested, especially the cellulose nitrates (Selwitz 1988). Thus, such a protocol makes for an unrealistic test.

Most published test results for coatings within the conservation field have focused primarily upon those used for outdoor sculpture. Tests typically involve exposure to "outdoor" environments such as sunlight, acid rain, and normal outdoor pollutant types and levels, and are usually performed on coatings applied to bronze, steel, zinc, lead, or iron substrates. Most of these tests include coatings and components other than those used for indoor silver artifacts such as paints, waxes, Incralac, benzotriazole and other corrosion inhibitors.

Here we focus on three coatings currently used by conservators for indoor silver protection: Agateen, a cellulose nitrate; and two acrylic polymers, Paraloid B-72 and Paraloid B-48N. Agateen has a long history of use as a silver coating (Heller 1983). However, some conservators fear deterioration problems with it, and have ceased to use it. Yet others still use it on a regular basis because of its advantageous working properties, and have not reported experiencing deterioration problems. The stability and reversibility of Paraloid B-72 are well-studied (Feller and Curran 1975; Feller 1984). Although these properties are somewhat affected by age and oxidation, B-72 is considered an excellent material for many conservation applications (Feller, Stolow and Jones 1985; Koob 1986). Most of the testing of B-72, however, has been for the purpose of assessing its use as a varnish for paintings or as a consolidant or adhesive for ceramics and glass. Its strong performance in those tests has lead to its selection as a silver coating. Unfortunately, tests of other applications cannot accurately predict performance as a metal coating since the substrate and demands on the coating are so different, and the percent solids generally differ. These factors can affect coating properties; and, of course, with other uses, corrosion development is not an issue. Paraloid B-48N is marketed as a coating for use on bare metal, but some conservators have avoided it because of alleged problems with yellowing and discoloration. Clearly, all three of these coatings currently in use by conservators need in-depth, objective tests for their performance when used on silver artifacts housed in an indoor environment.

The testing protocols developed in this study were aimed at maintaining relevance to actual conservation situations, while also incorporating new industrial testing techniques. Accelerated test methods were used to compare the relative merits of the three coatings in their ability to protect silver substrates against corrosive pollutants typically found in museums and historic houses. Since objects in museums and historic houses are not normally exposed to high levels of UV light, but rather are more likely to be exposed to elevated temperatures and high humidity, these tests combined the latter destructive factors, thus avoiding the extreme temperature that would decompose Agateen. It has long been noted in the literature than common environmental pollutants which are off-gassing products in storage or display case materials may affect coated metals (Oddy 1973; Padfield, Erhardt and Hopwood 1982; Hackney 1984; Donovan 1986; Hatchfield and Carpenter 1987; Hisham and Grosjean 1989; Nazaroff and Cass 1989; Druzik et al 1990; Grzywacz and Stulik 1991; Grzywacs and Tennent 1994; and Thickett, Bradley and Lee 1998). The tests therefore included exposure to common indoor pollutants such as hydrogen sulfide, sulfur dioxide, ozone, formaldehyde and acetic acid.

Although silver is very resistant to corrosion from most sources, it does react readily with sulfur in a reduced state of oxidation, as found in hydrogen sulfide, to form silver sulfide, the principal tarnish product found on silver. As has been reported in the conservation literature (Sease et al 1997), high levels (i.e., a few parts per million) of this tarnishing pollutant can develop inside display cases, off-gassed not only from case materials, but also from artifacts that may be housed with silver. Tightly sealed storerooms can also build up high levels of sulfur pollutants. To exacerbate the problem, high levels are not required to initiate tarnish; hydrogen sulfide can tarnish silver at concentrations as low as 10 parts per billion (Pope, Gibbens, and Moss 1968). Carbonyl sulfide, a dangerous tarnishing agent for silver, can also be released from wool and other keratinaceous materials found with artifacts, or materials used in construction of exhibit cases or storage units (Brimblecombe, Shooter, and Kaur 1992). Although reduced sulfur tends to be increased by indoor-generated pollutants, sulfur dioxide levels may be the result of entrance of outdoor-generated automobile pollution (Richey 1982). It is possible that sulfur dioxide attacks silver, along with hydrogen sulfide (Addicks 1940; Thomson 1965).

Since application error and difficulty are acknowledged causes of failure for silver coatings, a variety of shapes and surfaces were used in our testing program. Rather than using flat test specimens, bent L-shaped and engraved surfaces were used to mimic the types of surfaces conservators would normally need to coat and protect from tarnish. Both sterling silver and unalloyed silver were used. Coatings were either sprayed or brushed onto the test specimens. To provide a quantitative measure of corrosion (tarnishing) which might occur under either a sound or a failed coating, flat-surface electrical resistance atmospheric corrosion sensors made of silver were utilized. The results were also assessed visually, but incorporated such experimental design features as randomization, replication, controls, blind assessments, multiple assessors, and statistical tests. To quantify visual changes in the coatings themselves as opposed to changes in the silver substrates as tarnish developed, color changes of coatings were measured on glass tubes with a spectrophotometer after accelerated aging. Finally, information was gathered on actual coated objects in collections to compare the results with conservator's experiences, and to see how (and if) certain coatings have failed during service.

2. Methods

2.1 Coatings

The three coatings tested -- Agateen, Paraloid B-72, and Paraloid B-48N, were selected because they are currently in use as coatings for silver artifacts. They were prepared using protocols that mimic actual conservation applications.

2.1.1 Agateen

Agateen is a cellulose nitrate coating available as a proprietary mixed solvent manufactured by Agate Manufacturing Company. For use as a metal coating it is further diluted with lacquer thinner to about 10-15% solids by weight. While the long-term stability of cellulose lacquers has been questioned, many conservators select it for its good working properties. For example, Heller (1983) prefers it over acrylic polymers as a silver coating because he feels it has superior spray application properties, tends not to run, levels well, has a slower evaporating solvent, and produces a satisfactory surface quality in which the coating is essentially invisible to viewers of the artifact. We used Agateen Lacquer No. 27, diluted with 3 parts Agateen Lacquer Thinner No. 1, the concentration advised by the manufacturer.

2.1.1 Paraloid B-72

Paraloid B-72, manufactured by Röhm and Haas, is a copolymer of ethyl methacrylate and methyl acrylate. It is supplied as pellets and is prepared as a solvent solution; it is soluble in acetone, toluene, xylene, and lacquer thinners (de Witte et al 1978; Koob 1986; Röhm and Haas 1990). Based on recent research regarding variations in coating properties for an acrylic polymer dissolved in various solvents (Hansen et al 1991; Hansen 1994) xylene was chosen as the solvent. Paraloid B-72 has undergone much testing in the conservation field (Feller and Curran 1975; Feller 1981; Koob 1986), primarily for use as a varnish, adhesive, and consolidant. It has been found to be a very stable material, resistant to oxidation, light, hydrolysis and heat, maintaining transparency and reversibility for extended periods of artificial aging.

The B-72 was prepared as a 10% wt/vol in a 95% xylene and 5% butyl cellosolve solution. The butyl cellosolve (ethylene glycol monoethylene) is sometimes added by conservators as a leveling agent to reproduce the prized leveling quality of Agateen; otherwise it is difficult to apply this coating without bumps appearing on the surface.

2.1.3 Paraloid B-48N

Paraloid B-48N, also manufactured by Röhm and Haas, is a copolymer of methyl methacrylate and butyl acrylate. It was designed primarily for clear and pigmented coatings for metals, and is listed as having good adhesion, durability, toughness, flexibility, and weathering characteristics. It too is generally prepared as a solvent solution of dry powder pellets (Röhm and Haas 1990). Again xylene was chosen as the solvent, for fast evaporation (Röhm and Haas recommends either toluene or xylene).

The Canadian Conservation Institute (Down et al 1992) undertook natural aging of both Paraloid B-72 and B-48N in light and dark environments for a period of three to five years. In discoloration tests carried out for five years in dark conditions, B-48N exhibited less yellowing than did B-72. However, Feller (1981) found that acrylics containing butyl and amyl esters have a greater tendency to crosslink, so it was unclear which of the two acrylic coatings might be expected to perform the best. As with the B-72, B-48N was prepared as a 10% wt/vol solution, also in a 95% xylene and 5% butyl cellosolve solution.

2.2 Coating Application

Application protocols were chosen to reproduce the application methods commonly used by conservators. Most silver coatings are either brushed or sprayed on (Wharton 1997). Thus each coating was applied by both methods. Brushing was accomplished with a soft-bristled artist's brush (Figure 1). Spraying was performed using a Devilbis spray gun at 20 psi (Figure 2).

2.3 Substrates and Replicates

The form of test specimens was carefully considered to maintain as much relevance as possible to actual conservation situations. There was a desire to conduct a variety of tests, including assessment of visual changes, quantitative measurement of corrosion, and evaluation of changes occurring with the coatings themselves, in addition to corrosion formation. Therefore a variety of substrates were employed: bent specimens of sterling silver, fine silver coins, electrical resistance atmospheric corrosion sensors made of thin silver films, and glass tubes. The assembled test specimens represent a wide range of surfaces and shapes typically encountered with historic silver objects. A sufficient number of replicates for each substrate was included to assure accurate assessment of within- and between-group variation.

All test specimens (bent, coins, sensors and tubes) were marked with identifying numbers. Each specimen was then randomly assigned to a coating treatment using a random number table. This also allowed the specimens to be blindly evaluated as to which coating had been applied.

2.3.1 Bent Test Specimens

Some deterioration effects of coatings on collections objects are often more noticeable on inside or outside edges, and would not appear on the flat test specimens more commonly used in coatings performance tests. It has been noted in the corrosion literature (Carter 1982) that flat test specimens, although advantageous because of ease of coating application in a uniform manner and ease of assessment, are disadvantageous. One of the disadvantages cited is that coatings vary in thickness with the geometry of an irregularly shaped surface. On artifacts, there can be liquid run-off from edges and retention in recesses. With sprayed coatings thin areas can also result from shielding due to complexities of a shape. There may be differing degrees of work-hardening produced during finishing by varying amounts of polishing depending upon geometry, which may influence service performance of a coating. And, there may be unevenness of exposure to the corrosive environment with recessed areas retaining greater amounts of corrodent for longer periods, while the corrodent runs off more readily from sharply angled areas. Test specimens that more closely match the actual types of objects that will be coated in conservation practice are therefore preferable. To ensure that any edge effects or other variability due to coating application on complex artifacts would be detected, bent, L-shaped sterling silver specimens (Figure 3) instead of flat coupons were designed. These were 0.8 mm thick, and 1 square cm per side.

For each experiment, ten bent specimens were coated with each of the three coatings, for a total of 30. Of the ten for each coating, five were brushed and five were sprayed. Four specimens for each coating (two brushed and two sprayed) were left unexposed as controls, housed for the duration of the experiments in a desiccator. Two bent specimens were left uncoated, and were exposed to the same test conditions as the coated objects. These served as controls for the degree of tarnish that could be expected if no coating treatment were applied.

2.3.2 Coins

To detect any problems that might appear on flat surfaces with shallow design engravings, we also included silver coins in all tests. This also provided us with comparative tests on sterling silver (the bent specimens) as well as on silver unalloyed with copper (the coins, 99.95% silver).

For each experiment, four coins were coated with each of the three coatings (two by brushing and two by spraying), for a total of 12 test coins. Two additional coated coins were housed in the desiccator during the experiments, to serve as controls for untarnished initial appearance. Two uncoated coins were also exposed to the accelerated aging environment, to represent the maximum degree of tarnish that could be expected with no treatment.

2.3.3 Electrical Resistance Atmospheric Corrosion Sensors

To provide a quantitative measure of corrosion (tarnishing) which might occur under either a sound or a failed coating, flat-surfaced electrical resistance atmospheric corrosion sensors made of fine silver were utilized (Figure 4). Thin-film electrical resistance corrosion sensors were originally developed to evaluate the effectiveness of vapor corrosion inhibitors (Moore and Miksic 1995). The sensor consists of a thin metal film in serpentine pattern, with two electrical taps at each end and one at the center. It provides a corrosion measurement surface and a reference element coated with an insulating material. Changes in the ratio between the electrical resistance of the measurement element and the reference element of the sensor are related to corrosion (metal loss). These changes in metal loss, as a function of time, are related to a corrosion rate. The sensors are designed to measure metal loss of as little as 2.5 angstroms (Å), and are repeatable to plus/minus one angstrom; thus they can measure even very short-term changes in corrosion levels.

The electrical resistance sensors were used to evaluate each coating's ability to protect the substrate in our harsh environment, whether or not the coating remained intact. Resistance of these foil sensors is measured with a sensitive electrical bridge circuit. The data evaluated the degree of protection, even at or below the threshold of visual detection of tarnishing. Weight loss measurements of metal specimens cannot replicate this precision because the corrosion product (tarnish) film weighs more than the metal oxidized in the process, and removal of such films invariably involves the removal of some sound metal as well.

The sensors were brush coated with the same three coatings as were used on the test specimens (spraying would have provided less control in covering the area of the corrosion measurement surface). For each of three experiments, we used four sensors with each of the three coating materials, for a total of twelve sensors per experiment (two more were left uncoated for comparison). These were exposed along with the other test specimens, and resistance readings taken periodically to ascertain any metal corrosion which may have occurred. The advantage of such sensors is that corrosion can be measured under coatings without disturbing the coatings; it is well known (Carter 1982) that damage to a metal substrate can easily occur without the development of visual corrosion products.

2.3.4 Glass Tubes

For each experiment, four glass tubes were coated with each of the coatings under study. Two for each coating served as controls, and two underwent the same accelerated aging as did the test specimens. The purpose of these glass tubes was to serve as a measure of the deterioration of the coating itself under accelerated aging, without regard for the development of corrosion on a silver substrate. These tubes were to be used for spectrophotometer readings to evaluate color change in the coatings as a result of accelerated aging-induced deterioration. Since applying the coatings to these tubes by spraying or brushing was quite difficult, they were instead dipped in each coating.

2.4 Accelerated Aging Environments

Accelerated aging was performed in simple chambers that could be reproduced in any conservation laboratory (Figure 5). Two chambers were used, one for a wet environment and one for a dry environment; a movable sample holder was constructed so samples could easily be rotated between the two chambers minimizing the handling. Each of the two chambers was constructed using a sealed 20-gallon glass aquarium, set into an insulated plywood box. The removable sample holder was built of Plexiglas; all samples were hung or set into place on this holder, and moved at the appropriate periods from the wet environment chamber to the drier one.

In the wet environment chamber, conditions were maintained at 50° C and 100% RH. A shallow pan of water provided the RH; and heat was introduced with a hot air gun (hair dryer) set into a hole cut into the plywood box (Figure 6). The second chamber was maintained at typical room temperature and RH conditions. Room conditions were not strictly controlled, but were constantly measured (with RH between 50-60% and temperature between 20-21° C).

Our accelerated aging protocols were designed to mimic, as much as is possible, the environmental factors to which silver objects in museums and historic houses are likely to be exposed. In the indoor environment, objects are not normally exposed to high levels of UV light, but may be exposed to elevated temperatures and high humidity; thus our test combines these latter destructive factors but does not include elevated UV exposure. Since it is known that common environmental pollutants and off-gassing products in storage or display case materials can affect coatings, our tests therefore include exposure to common indoor pollutants such as hydrogen sulfide, sulfur dioxide, ozone, formaldehyde and acetic acid.

Conservators have hypothesized that there is a synergistic effect between a mixture of pollutants, such as might be typically found in a storage or exhibition environment, and fluctuating temperature and humidity. Our accelerated tests, therefore, expose specimens to a "cocktail" of volatile pollutants, as well as to fluctuating temperature and relative humidity that may cause stress on the coatings.

The following pollutants were produced and introduced into the first test chamber with elevated temperature and RH:

(1) H_2S, produced with 1% Na_2S, using 1 gram in 300 mL water with pH adjusted to 7.0; the entire solution was placed in a 500 mL beaker inside the test chamber.

(2) SO_2, produced using 0.01 gram of $NaHSO_3$ plus 10 drops of 3% H_2SO_4 in a small weighing boat inside the test chamber.

The following pollutants were introduced in the second, dry test chamber, with room temperature conditions:

(3) Ozone was produced by running an ozone generator at the lowest output for 3 minutes at about 10 ppm into the test chamber, producing an ozone level of about 1 ppm (O_3 will decompose to O_2 in the test chamber). Ozone can have a direct oxidative effect on coatings, so does not need the high humidity to cause deterioration.

(4) Acetic acid, introduced with 1 mL of 10% acetic acid dispensed into filter paper laying in the bottom of the test chamber.

(5) Formaldehyde, introduced as 1 mL of 10% formaldehyde dispensed onto filter paper laying in the bottom of the test chamber.

The level of pollutants present in the atmosphere inside the chambers were monitored using Dräger diffusion tubes. Minimum detection limits include 1.3 ppm for hydrogen sulfide, 0.63 ppm for sulfur dioxide, 0.5 ppm for ozone, 1.3 ppm for acetic acid, and 0.04 ppm for formaldehyde.

The order of placement of test specimens within the chambers was randomized, so that if there were any pockets of high or low concentration of pollutants, temperature, or RH, no single coating would be unilaterally affected. This randomization was achieved by placing specimens in numerical order, since the numbered coupons had been randomized during coating treatment.

2.5 Methods of Evaluation

Coating performance was assessed both visually and quantitatively. Statistical tests were used to help evaluate both methods of assessment.

2.5.1 Visual Assessment

For bent specimens and coins, the objects were removed from the test chamber holder in the same randomized order in which they had been placed. Using the uncoated controls as one end of the scale (maximum tarnish) and the coated specimens kept in a desiccator as the other end of the scale (original appearance of freshly coated objects), the specimens were ranked from best to worst. Biased judging was avoided by the use of numerical codings, so that judges were unaware of which coating had been applied to each specimen. For the first two experiments, multiple independent judges ranked all specimens. Since there proved to be no significant difference between their rankings, the multiple rankings were deemed unnecessary and were dropped for the final experiment.

One of the factors considered here are presence of visible corrosion (tarnishing) under the coatings, usually appearing as localized or an overall black film; as well as changes in the coating itself which may include cracking, peeling, blistering, hazing, or discoloring. Both coating deterioration and silver tarnish may be present. Aesthetic parameters are considered as important as functional parameters, since cultural artifacts are intended to be viewed by the public, and any change in appearance that detracts from seeing the object as was intended by those who originally made it is unacceptable.

Analysis of these data were conducted using a standard statistical test designed for two-factorial experiments (coating and application method), a two-way analysis of variance (ANOVA) (Dixon 1988; Reedy and Reedy 1994). The null hypothesis is that all group means are equal. A test statistic is calculated using the observed divided by the expected variance of the group means, as computed from group number, sizes, and variances. The *p*-value is the probability of getting a test statistic as extreme as that observed, and tells whether or not the null hypothesis is supported. With a two-way ANOVA, the interaction effects could also be statistically evaluated (e.g., whether the effect of application method varies significantly from one coating to another).

2.5.2 Quantitative Assessment

The electrical resistance atmospheric corrosion sensors provided a quantitative measure of angstroms of metal loss, or loss of conductivity as metal was converted to corrosion products. Data interpretation for the sensor data was done by analysis of variance using the same BMDP program. Since only one application method was present, there was no need to check for any interaction effects, and thus a one-way ANOVA was used.

The coated glass tubes were assessed using a spectrophotometer to measure the change that occurred during accelerated aging exposure, measuring different wavelengths: 470 nm (blue), 580 nm (yellow) and 650 nm (red). The instrument was calibrated initially by setting the light transmission through an uncoated glass tube at 580 nm to "100". A medium sensitivity setting was used throughout.

2.5.3 Reversibility

In conservation practice, reversibility of any treatment is considered extremely important. The Code of Ethics of the American Institute for Conservation stresses this factor, and urges conservators to avoid using any materials that cannot be removed in the future if that becomes necessary (AIC 1998). In the case of protective coatings for tarnishable metals, this is a significant concern because experience has shown that even the best coatings eventually will have to be removed and replaced. Any coating which cannot be removed without risking damage to the substrate is, therefore, clearly unacceptable.

To evaluate comparative reversibility, each coating was tested with both acetone and xylene. A brief swabbing with cotton or dipping in these respective solvents needs to completely remove the coatings in a relatively short period of time, since one would never want to expose an artifact to a strong solvent for extended periods. Therefore, the specimens were first swabbed with solvent to observe changes in solubility which may have occurred as a result of the artificial aging. They were then partially immersed in solvent for a period of up to ten minutes and the degree of coating removal observed.

3. Experiments

3.1 Experiment 1

The original plan had been to leave the test specimens in the wet chamber (with the hydrogen sulfide and sulfur dioxide) for six days, then transfer them to the dry chamber (with ozone, formaldehyde, and ascetic acid) for one day, to dry out and stress the coatings. This alternating exposure schedule was intended to be repeated for several months. However, exposure to the sulfur pollutants was overwhelming, and caused noticeable to severe tarnishing of many test specimens by the end of the first six-day period. The level of H_2S in the test chamber fluctuated, up to 7 ppm; SO_2 was at a level of about 1 ppm. Experiment 1 was halted at this point, and all test specimens were evaluated for their ability to protect the silver from sulfur compound exposure.

The bent specimens and coins were cleaned and degreased, then recoated following our established protocols. New electrical resistance sensors and glass tubes were coated as before.

3.2 Experiment 2

3.2.1 Experiment 2A

The accelerated aging procedure was repeated with sulfur pollutants removed from the pollutant mix, to check for any affects the other pollutants might have, and to see how well the coatings performed under repeated wetting and drying. The alternating exposure schedule as described in Section 3.1 was conducted for three months. During this second experiment, pollutant levels were maintained at about 1 ppm for ozone, 10-25 ppm for acetic acid, and 5-10 ppm for formaldehyde. All visual and quantitative assessments were then performed.

3.2.2 Experiment 2B

The same test specimens from experiment 2A were then placed back into the wet chamber, and exposed to six days of high levels of hydrogen sulfide (3 ppm, without sulfur dioxide). The purpose of this exposure was to check whether or not aging of the coatings had an effect on their relative resistance to tarnishing by hydrogen sulfide.

4. Results

4.1 Experiment 1

The results of the two-way ANOVA test for visual differences between bent specimens is given in Table 1. In this case, 10 replicates for each of the three coatings (5 sprayed and 5 brushed) were ranked by three different individuals. Rankings were from best (least corroded, and thus with better protection offered by the coating) to worse (most corroded, worse protection offered by the coating). There were large differences visible between specimens (Figure 7).

Agateen was clearly the best coating for protection against sulfur exposure. The difference between it and the other two coatings is statistically significant ($p = 0.00$). The other two coatings are statistically similar to each other, although visually B-48N performed slightly better than did B-72. For all three coatings, spraying on the coating appears to be better for corrosion protection than brushing, and the difference is statistically significant ($p = 0.00$). There is a slight interaction effect, with the spraying versus brushing results a bit stronger for Agateen than for the two acrylics, but this difference is not statistically significant (which means that given the within-group variation, the between-group variation is not significant).

For the visual assessment of coins, the same ranking and statistical analysis procedures were performed. The results are given in Table 1. Again, Agateen was clearly the best-performing coating for protecting against sulfur exposure. The difference between it and the other coatings was statistically significant ($p = 0.00$). As before, the other two coatings were relatively similar in performance. Sprayed coatings and brushed ones showed no statistical difference, and no interaction effects were observed.

For the electrical resistance sensors, a baseline reading was taken prior to exposure to sulfur. At the end of the one week period, the sensors showed that Agateen provided better protection against tarnish from sulfur than did the other two coatings (Table 1). The difference in angstroms of metal lost was unexpected: for the four Agateen replicates, the average loss was 46 angstroms; versus an average of 190 for the B-72 replicates and 329 for the B-48N replicates. An analysis of variance shows this difference to be statistically significant ($p = 0.00$)

For the coatings applied to glass tubes, none of the three coatings showed a measurable reduction in light transmission prior to exposure to the "polluted" test atmosphere. This was true at all three wavelengths. From this it was concluded that all three candidate coatings are quite clear and transparent as applied.

After the first exposure period in high levels of hydrogen sulfide, all tubes showed some degree of white clouding to the naked eye. However, those coated with Agateen were relatively clear, while those coated with B-72 and B-48N were relatively opaque. Monochromatic transmission readings showed clear differences among the coatings, with the B-72 and B-48N coatings exhibiting a reduction in transmission of 16-26% versus the unexposed controls. The Agateen coating, on the other hand, showed only a 3-4% reduction as a result of the same exposure.

These results indicate that the high sulfur atmosphere is attacking the coatings themselves, as well as the underlying metal. All three coatings were easily reversible in acetone and/or xylene after the conclusion of the experiment.

4.2 Experiment 2A

The bent specimens and coins were assessed visually by the same protocols used in experiment 1. The results were similarly statistically analyzed by a two-way ANOVA as described above. Results are summarized in Table 1.

For the bent specimens, Agateen had a slightly lower overall score (indicating less tarnish) than did B-72, and B-48N; however, the differences were not statistically significant ($p = 0.70$). In contrast, application method was significant ($p = 0.03$), with brushing providing greater protection than spraying. There were no interaction effects between coating and application method.

For the coins, although not as dramatic in appearance as with the first experiment, Agateen again performed better ($p = 0.00$) than the other two coatings. There was no significant difference between B-72 and B-48N. Again, there was a significant difference overall between spraying or brushing ($p = 0.02$), with spraying providing better results. There were no interaction effects.

The electrical resistance data showed no serious corrosion development for any of the coatings upon exposure to this second environment (no serious loss of metal), and there is no difference in corrosion protection between coatings. The visual differences, then, may be due more to changes in the appearance of the coatings themselves.

New glass tubes had also been coated. Tubes that sat for the duration of exposure outside of the test chamber were used to separate the effects of time versus pollutants and cycling RH. These control tubes showed no measurable change in monochromatic transmission. For the tubes that underwent the three-month accelerated aging regime, all three coatings showed minor losses in light transmission, ranging from 12 to 15 % at 470 nm, 9 to 12 % at 580 nm, and 7 to 10 % at 650 nm. The changes observed for B-48N were somewhat higher than for the other two coatings; but all observed changes were small compared with those in Experiment 1. This result indicates that visual changes in the coatings themselves may be due more to incipient cracking and peeling.

Table 1 *Results*

		Applic.	Coating, Mean Values*			P-Values**		
Experiment	Substrate	Method	Agateen	B-72	B-48N	Coating	Method	Interaction
1	Bent	Brush	8	23	20			
		Spray	3	21	18	0.00	0.00	0.08
	Coin	Brush	4	9	6			
		Spray	3	8	9	0.00	0.45	0.18
	ER sensor	(Brush)	46	190	329	0.00	--	--
2A	Bent	Brush	10	14	12			
		Spray	18	16	23	0.70	0.03	0.42
	Coin	Brush	2	11	10			
		Spray	2	6	6	0.00	0.02	0.17
	ER sensor	(Brush)	94	119	99	0.65	--	--
2B	Bent	Brush	13	17	17			
		Spray	3	26	17	0.00	0.75	0.01
	Coin	Brush	4	7	5			
		Spray	2	11	8	0.09	0.36	0.36
	ER sensor	(Brush)	11	69	75	0.00	--	--

*Mean values are of ranks for bent specimens and coins, delta angstrom loss for ER sensors. Replicates are 10 for coating on bent, 4 on coins, 4 on ER sensors; and 5 for method on bent, 2 on coins.

**Statistically significant p-values are generally considered to be those at levels of .05 or below.

4.3 Experiment 2B

These results are also summarized in Table 1. For the bent specimens, Agateen performed significantly better (p = 0.00) than the other two coatings as a protective barrier against sulfur. For the coins, Agateen had a slightly lower score (less tarnish), although the difference is not statistically significant (p = 0.09). For B-48N and B-72 no differences were found between brushing and spraying for either test specimen type. For Agateen alone, spraying afforded better protection than brushing.

Sensors left from Experiment 1 were also re-exposed to this second sulfide atmosphere (except for one sensor that was destroyed in an attempt to see if it could be cleaned for re-coating). These results show a statistically significant difference between the coatings (p = 0.00), with Agateen causing less corrosion. The numerical values of additional metal loss were lower for all coatings than they were in the first exposure test, ranging from 8-104 angstroms (versus 11-388 angstroms). Again, all coatings were easily reversible after the conclusion of Experiment 2A/B.

5. Discussion

The primary objective of the experiments described above was to identify which of the three coatings performed the best. Indications of good long-term protective effects would include both serving as an effective barrier to harmful pollutants, and remaining intact through a variety of environmental stresses. Secondarily, we were interested in seeing if spraying or brushing made a difference and whether the coatings behaved differently on sterling silver bent coupons than with the engraved fine silver coins.

5.1 Experiment 2A

After experiment 2A, involving changes in RH and temperature and exposure to a variety of pollutants not including sulfur, most of the coatings were in good condition. However, a few were observed to be peeling along the edges of the bent specimens. Those that ranked worst showed slight yellowing of the coating. Those ranked highest were still a vibrant shiny strong silver color, with no yellowing or peeling. Visually ranking of the best and worst were easier than those in the middle, because there were few distinguishing differences between specimens.

For the bent specimens, all three coatings performed similarly in this second accelerated aging experiment with sulfur pollution removed. For the coins, however, Agateen showed less visual change. It is possible that this difference between performance with the bent specimens and coins may be due to differing effects of surface geometry, or to differences in composition of sterling silver versus fine silver.

Brushing was found to provide significantly better protection overall for the bent specimens, but not for the coins. It is possible that with the surface geometry of bending and extensive edges, spraying may sometimes lead to areas of incomplete or too thin coating coverage, which can be a significant problem after conditions of repeated long-term environmental stress. Electrical resistance data show that no serious corrosion development occurred, and there was no significant difference between coatings. The spectrophotometer readings of the coated glass tubes also showed that no major change occurred in light transmission through the coatings themselves. Thus any observed visual change may be mainly the effect of the slight cracking and peeling of the coatings from the substrates.

5.2 Experiments 1 and 2B

We can conclude that Agateen is distinctively the superior coating under exposure to high levels of sulfur. It shows the least deterioration, and provides a far better protective barrier against sulfur-induced corrosion. The performances of B-72 and B-48N are similar to each other, and it is not clear at this stage which would outperform the other. If protection against sulfur is a major concern, then Agateen is the recommended coating. Since Agateen also has handling and visual properties that many conservators prefer, this finding would appear to be a positive one.

After both experiments, the overall darkening of the silver on many test specimens (Figure 8) was considered to be failure. Electrical resistance sensors and coated glass tube analyses show that both tarnish development and increased coating opacity contribute to this visual change. In some cases where visible spots of tarnish developed, coatings were peeling. The peeling, however, was minor, and could perhaps be in part due to the tarnish disbonding the coating from below.

Although the electrical resistance sensors showed less metal loss for Agateen than for the two acrylics after both hydrogen sulfide exposures, that degree of loss was much less for Experiment 2B than it had been for Experiment 1. It is possible that this is due to somewhat lower concentrations of hydrogen sulfide, to the absence of sulfur dioxide, or perhaps the development of a very thin tarnish layer that may slow down subsequent rates of tarnishing. Still, the results of the first experiment with a high-sulfur atmosphere were replicated after the coatings had been subjected to three months of accelerated aging, and Agateen remains the better barrier against hydrogen sulfide relative to the other two coatings.

In these experiments, the only significant difference in application method for all coatings was seen on the bent specimens of Experiment 1, where spraying afforded better protection. Perhaps it produced a slightly thicker, more uniform coating, for better overall coverage, which helps protect the metal from hydrogen sulfide. For Experiment 2B, the improvement with spraying occurred only with Agateen.

Although spraying was found to be better for hydrogen sulfide protection, we found that brushing was better for the bent coupons of Experiment 2A. It may be that under longer-term conditions of environmental stress, sprayed surfaces will not hold up as well where there are many bends and edges. Since most artifacts have a complex geometry, brushing (with Agateen), while taking care to ensure there is complete coverage and a relatively thick coat, may be the best approach.

5.3 Comparison of Results to Real Case Studies

The results of this laboratory study were compared to observations of coatings after natural aging of historic silver objects. These observations included those of the objects conservator on our research team (D. Long) and those of other conservators as reported in the literature and on an online discussion forum.

Agateen has been used longer and more often in the conservation field as a silver coating than have the two acrylic coatings. No one has reported overall tarnishing of silver coated with Agateen, supporting our findings regarding impermeability. There have, however, been conflicting reports regarding its longevity. On objects coated with other cellulose nitrate lacquers, it has been observed that sometimes a deteriorated coating does not peel from the surface. Instead, as it shrinks, it leaves protection in small islands surrounded by uncoated surfaces that corrode rapidly.

However, the primary cause of coating failure observed with cellulose nitrate lacquers (as with any other coating used for a museum object) has been error in application; natural deterioration is also exacerbated by application errors. These errors include inadequate surface preparation; uneven application, with some coating areas being extremely thin; or areas being missed altogether, which is especially common in areas of complex geometry.

Heller (1983) was an early and strong advocate for Agateen, based on the ease with which it is possible to obtain a desirable quality of surface appearance. He reported observing Agateen-coated silver objects still in excellent condition after as long as 15 years, with no signs of deterioration. In trying to use B-72 as a silver coating, Heller found that solvents tended to evaporate more slowly, that spraying was especially difficult, and that the coating had a tendency to run and not level properly. The lengthy drying time made handling the object during application difficult, and the coating often remained soft and susceptible to fingerprints, lint from gloves, or to dust.

An interesting discussion among conservators regarding their experiences with Agateen, other cellulose nitrate coatings, and B-72 appears on the electronic discussion list of the American Institute for Conservation Objects Group (Objects Specialty Group Discussion List 1997). Many conservators reported using Agateen, because of its many positive qualities. One noted it is very easy to achieve a beautiful surface by brushing or spraying using Agateen. Another reported using it for protection of indoor metals because it is less vapor-permeable than the acrylics such as B-72, and because it dries in such close conformation with the surface it is applied to, unlike acrylics that tend to leave an "orange peel" surface.

Another conservator who reports having tried a wide variety of lacquers, spray applied, on indoor silver has found that Agateen is by far the most "forgiving" so that there is rarely any problem with either the "orange peel" look or with bubbles forming on the surface. This was found to be an especially useful property for the common situation in which coatings were applied by less experienced technicians, and saved retreatment of unsatisfactory work. Here the impermeable quality of Agateen was also crucial, because the collection it was being applied to was housed in an institution with a severe sulfur pollution problem. One conservator noted that Agateen remains soluble in acetone, and so can easily be removed if necessary. Several conservators had experienced easy removal of Agateen coatings that were 10-12 years old, finding it to be very soluble in acetone, even when degraded.

One conservator has retreated hundreds of pieces of silver that were lacquered with cellulose nitrate lacquers in the late 1950's through 1970's. He found that those aging lacquers exhibited brittle losses, underfilm tarnish, discoloration, and often had small patches of degraded lacquer which could not be removed without extremely aggressive localized mechanical abrasion which also removed some metal. However, it was unclear if any of those lacquers were Agateen, or one or more of the many other cellulose nitrate lacquers that have been on the market, such as Frigilene (Plenderleith and Werner 1971). His experience with acrylic coatings was that they worked well for copper alloys and ferrous metals, while silver was quite reactive, with the lacquer layers peppered with tiny spots of sulfide corrosion.

Some members of the discussion group felt that the positive qualities of Agateen outweigh any potential need to remove and reapply it at a later time. One felt that it would need to be replaced in about 20 years, as it might discolor before the film actually breaks down. However, another felt that it is difficult to justify a treatment that would require coating replacement every 20 years, as many institutions do not have adequate resources for retreatment.

Selwitz (1988) discussed the chemistry and properties of cellulose nitrate, and clarified why it is appropriate for use as an indoor coating. He noted that there is no reliable documentation regarding exactly how long such coatings should be expected to last; but that cellulose nitrate cast into films and kept out of bright light appears to have held up well for over 60 years. He noted that studies showing lack of stability of cellulose nitrate involved light exposures equivalent to 100-150 years in a typical museum situation; and used very high temperatures which cause decomposition of cellulose nitrate, especially in conjunction with surges in RH. The modes of decomposition observed in such experiments would not be observed in conditions of actual use of a cellulose nitrate coating on silver. These findings were supported by recent research on degradation of cellulose nitrate adhesives (Shashoua, Bradley, and Daniels 1992), where the degradation was found to be substantially retarded by the plasticizer, and a lifetime of 50-100 years was hypothesized as probable under normal museum conditions.

Sease et al (1997) have noted that application method can be very important, as even an impermeable lacquer can allow tarnish to penetrate if there are areas of incomplete coverage, pores in thin lacquer, or interruptions along edges. They observed black tarnish appearing on lacquered silver objects within six months of being placed in exhibit cases where sulfur had off-gassed from both case materials and from other artifacts housed with the silver ones. The black crystals appeared to be growing at breaks in the lacquer; crystals then pushed off sections of the coating, allowing a larger area of tarnish to form. They recommend applying multiple layers to ensure that the coatings are flawless. Other conservators also follow this procedure of applying two layers of a coating brushed or sprayed in opposite directions when possible, to better ensure complete coverage, no matter which coating is used or whether it is brushed or sprayed (Wharton 1997).

However, at one institution, the experience of conservators has been that B-72, whether brushed or sprayed on, in two or sometimes even three coats, cannot protect silver in the presence of sulfur pollutants. They have found that even with multiple coats B-72 is permeable to any hydrogen sulfide in the display (Podany 1998).

No matter how stable a coating, if it is permeable to hydrogen sulfide then a dangerous situation is set into place. Environmental conditions in exhibition and storage spaces must be constantly and carefully controlled to prevent accumulation of the pollutant at levels of 0.10 ppb or more. Higher levels, or combinations of hydrogen sulfide with other sulfur pollutants, must be completely avoided even for brief periods of time or tarnish is likely to develop. Then not only must the coating be removed and reapplied, the tarnish itself must be removed. This usually requires use of acidified thiourea (a known carcinogen) to chemically dissolve the silver sulfide, or abrasives (Wharton 1997). The latter create fewer health hazards, but can be extremely time consuming, and will remove some of the silver.

6. Conclusions

Our experiments clearly show that Agateen is much less permeable to hydrogen sulfide than are Paraloid B-72 and Paraloid B-48N. This fact holds true both for freshly coated silver and for those with deteriorating coatings. Where no deterioration has occurred, Agateen is remarkably impermeable to even extreme levels of hydrogen sulfide and sulfur dioxide; our findings coincide with field observations that have been made by conservators. Since levels as low as 0.10 ppb of hydrogen sulfide are known to tarnish silver, impermeability to this pollutant is an important consideration in coating selection. Removal of tarnish is a long and involved task, to be avoided if at all possible.

In an accelerated aging environment containing cycling RH and temperature, along with a pollutant mix, there was no significant difference in performance of the three coatings on the bent sterling silver specimens. All three began to peel and develop losses along edges and corners, and all three coatings developed noticeable discoloration. On fine silver coins Agateen continued to perform better. However, the overall black tarnish seen during exposure to sulfur pollutants did not appear under these experimental conditions. Electrical resistance measurements and spectrophotometer data indicate that the observed difference may be mainly due to differences in incipient cracking and peeling of the coatings.

Conservators frequently express concern over the stability of Agateen because of problems associated with other cellulose nitrate products, but primarily because of De Witte's 1973 studies which indicated cellulose nitrate coatings were much less stable than acrylics such as B-72. However, following the suggestion of Selwitz (1988) that the high temperatures used in those experiments would create problems not observed under normal use, less extreme aging conditions were used for our experiments. Our results indicating relative stability of Agateen when used in an indoor environment coincide with many observations reported by conservators who use this coating; however, based on such observations these results should not be extrapolated to other cellulose nitrate coatings. The mix of additives found in individual products may have important effects; and the known detrimental effects of ultraviolet radiation on cellulose nitrate should preclude its use in an outdoor environment.

Agateen has distinct advantages in ease of application and in surface appearance on silver. Given its performance in these tests, it clearly should have a place in the conservation of silver objects. B-72 and B-48N have more equivalent stability, reversibility, and protection from tarnish in the absence of sulfur pollutants. Their problematic working properties may be adjusted by changes in solvent, additives, or other aspects of formulation. However, they should only be used in an environment that can be guaranteed to be free of sulfur pollutants, or they will probably fail. It is possible that multiple layers of coating will ameliorate the problem with permeability, but it remains to be tested whether or not that will be effective and what the optimum thickness or number of layers would be. Reported experiences of conservators indicate that two to three layers as normally applied in conservation may not be sufficient for hydrogen sulfide-permeable coatings.

For any coating, inadequate surface preparation and applicator error is often the source for the initiation of tarnish. In our experiments we found that where there are many bends, narrow edges, and other geometric complexities, brushing rather than spraying provided better coverage for those difficult areas, and thus reduced peeling and cracking problems under environmental stress. But for hydrogen sulfide protection, spraying was sometimes more effective, perhaps resulting in an overall thicker and more uniform coating. To be safe, some conservators routinely apply two coatings to ensure better coverage; this is clearly a prudent step.

Many other coatings are available from manufacturers, and may produce superior results to those tested here. In addition to testing B-72 and B-48N applied in multiple layers, supplementary research could be done to evaluate other coatings for protection of silver housed indoors. Conservators having a wide repertoire of materials and techniques from which to choose for a specific situation, rather than a limited number of tested coatings, should be our ultimate goal.

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Suppliers

Electrical resistance sensors: Model 610 High Sensitivity Atmospheric Corrosion Sensor, Rohrback Cosasco Systems, Inc., 11841 East Smith Avenue, Santa Fe Springs, CA 90670.

Dräger tubes: Fisher Scientific, 711 Forbes Avenue, Pittsburgh, PA 15219-9919.

Agateen Lacquer #27 and #1 Lacquer Thinner: Agate Manufacturing Co., 11-13 Forty-third Road, Long Island City, New York, 11101.

Paraloid B-72 and B-48N: Röhm and Haas Company, Independence Mall West, Philadelphia, PA 19105.

Butyl Cellosolve: Aldrich, 1001 West Saint Paul Avenue, Milwaukee, WI 53233.

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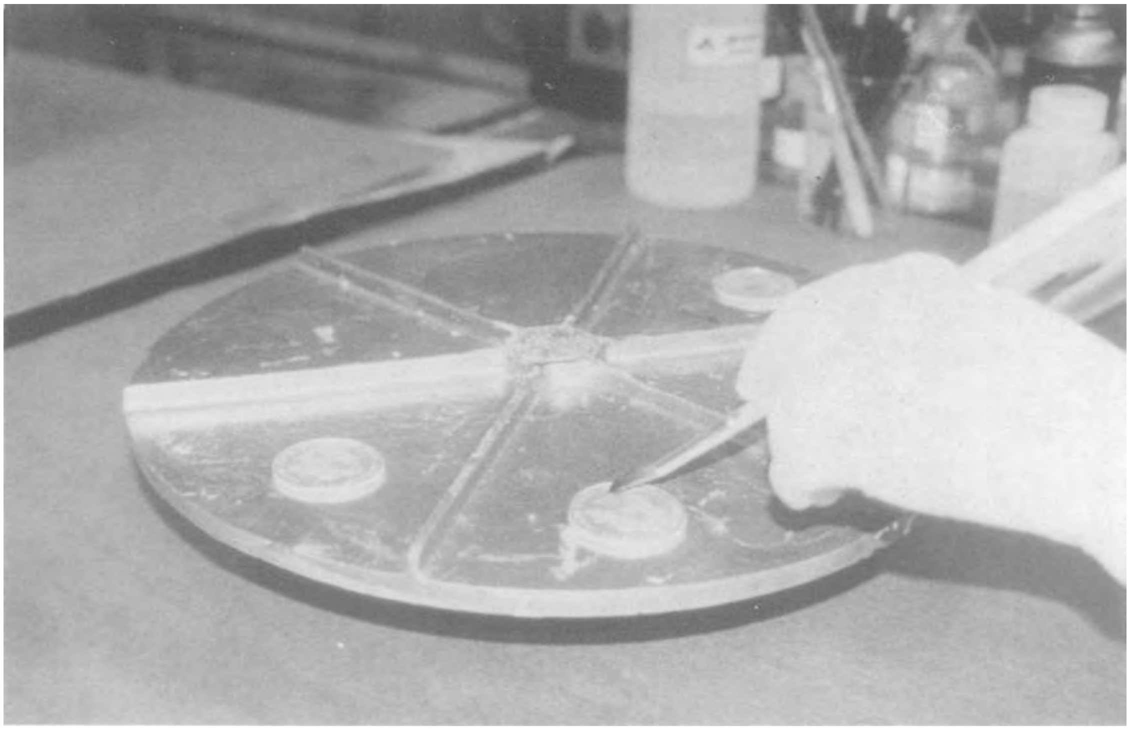

Figure 1. Brushing on coating with soft-bristled artist's brush.

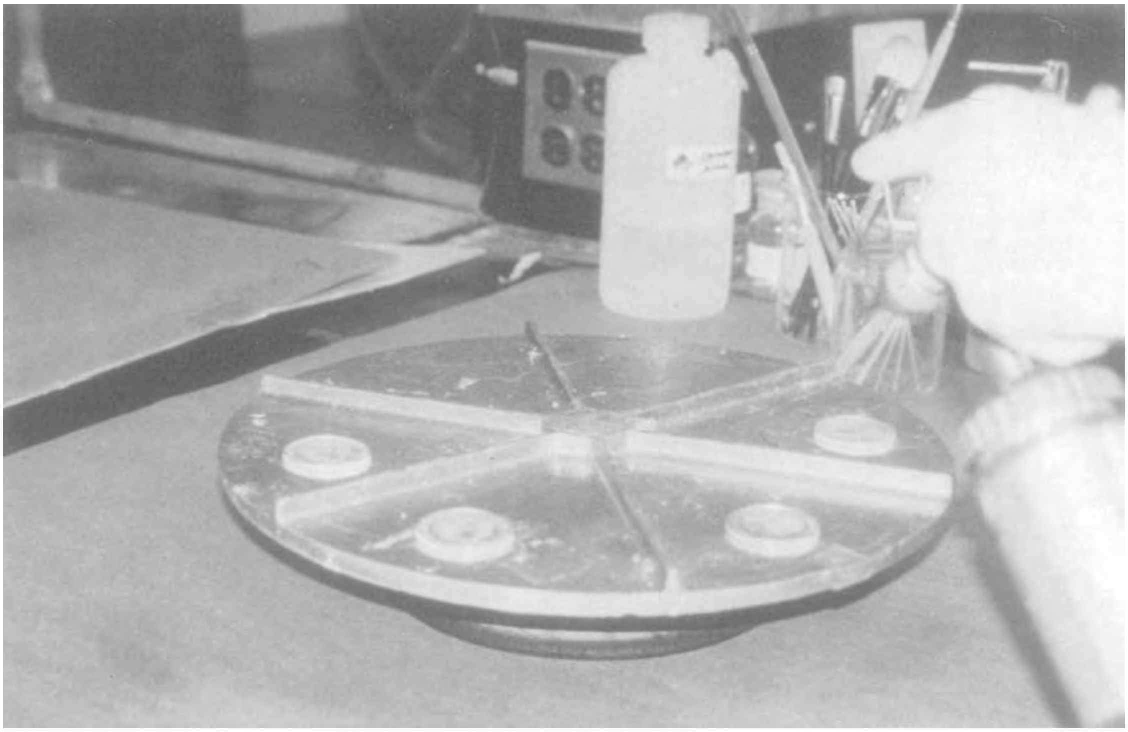

Figure 2. Spraying on coating with Devilbis spray gun at 20 psi.

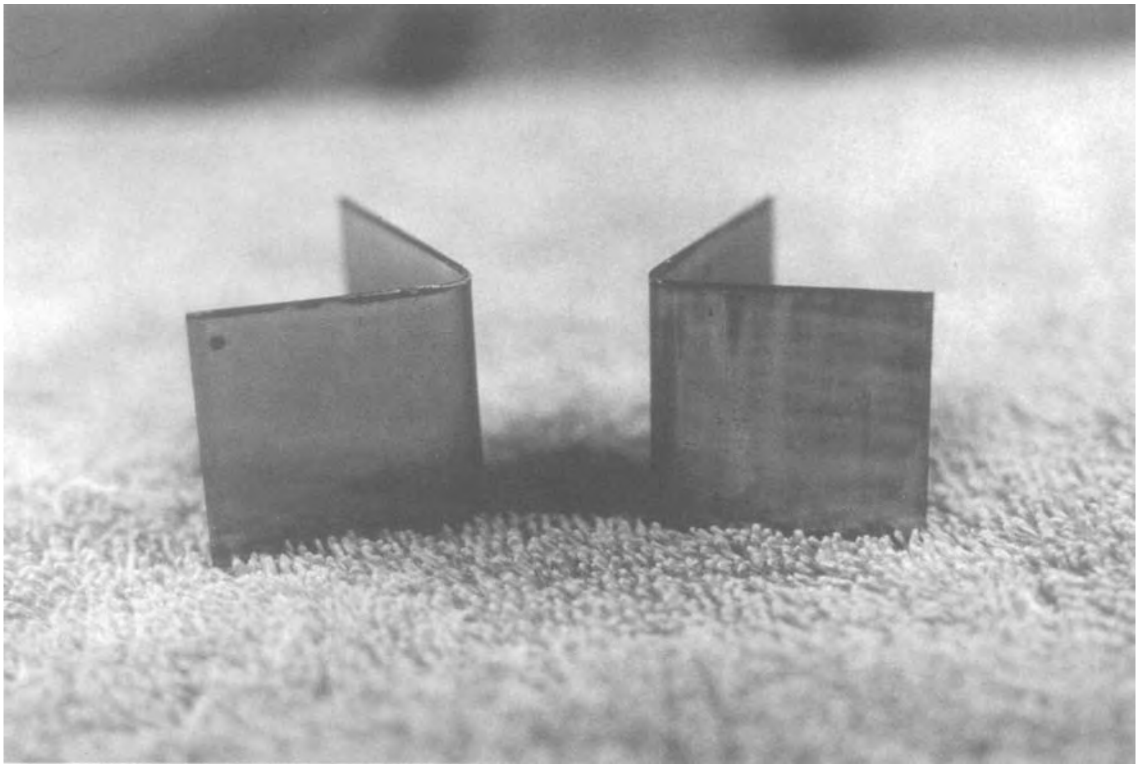

Figure 3. Bent sterling silver test specimens.

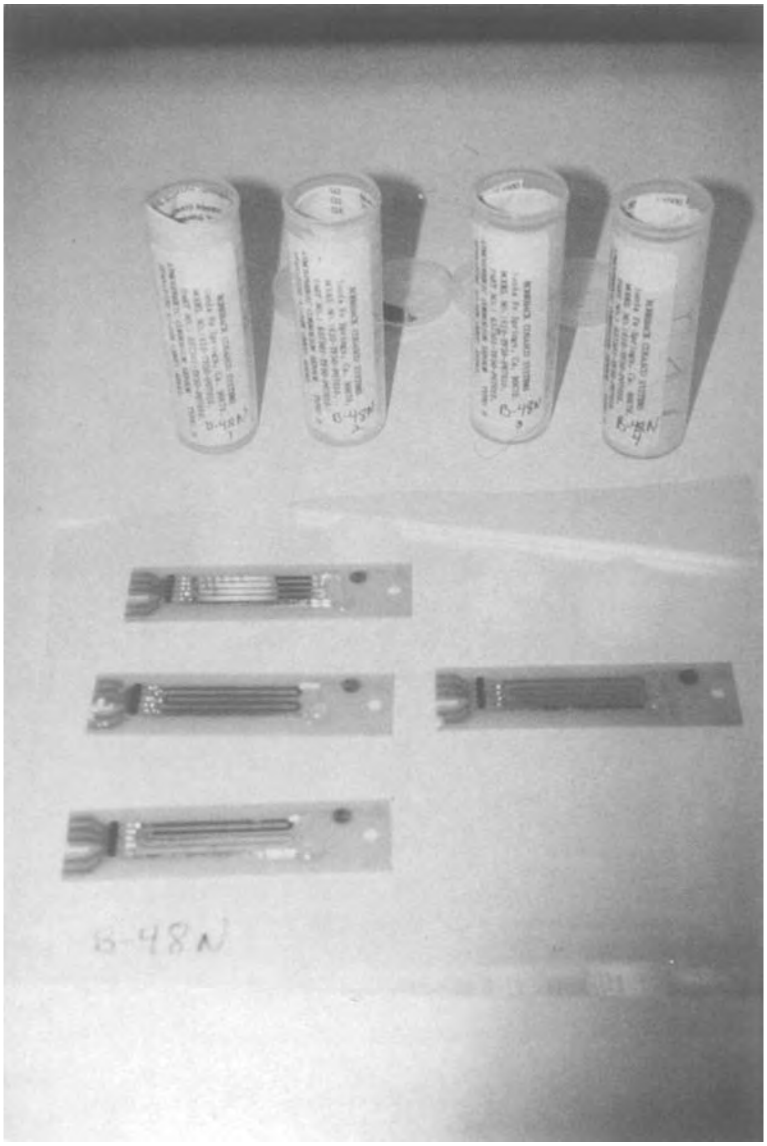

Figure 4. Electrical resistance atmospheric corrosion sensors.

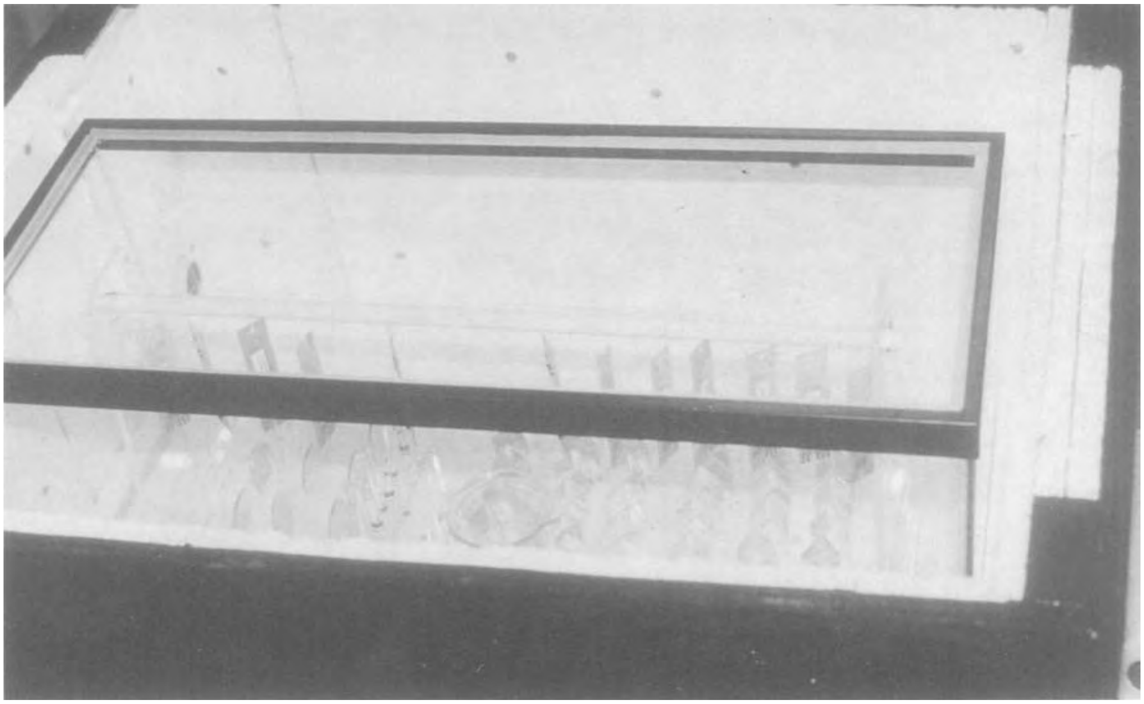

Figure 5. Accelerated aging chamber with removable sample holder in place.

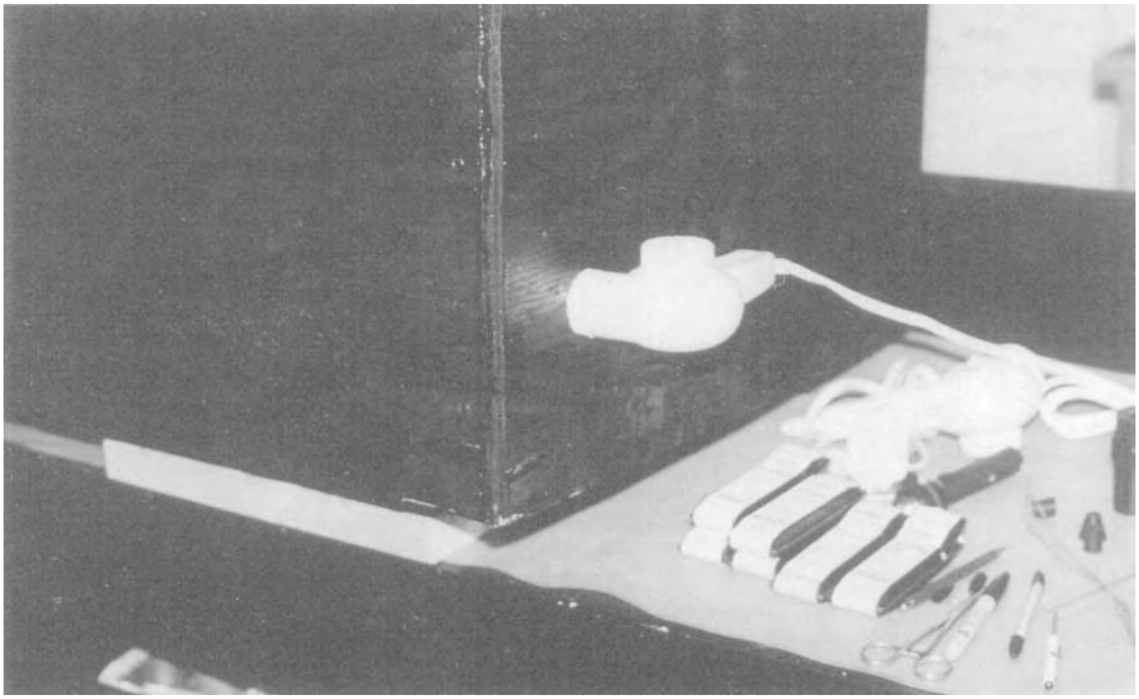

Figure 6. Hot air gun set into hole in plywood box surrounding the glass chamber.

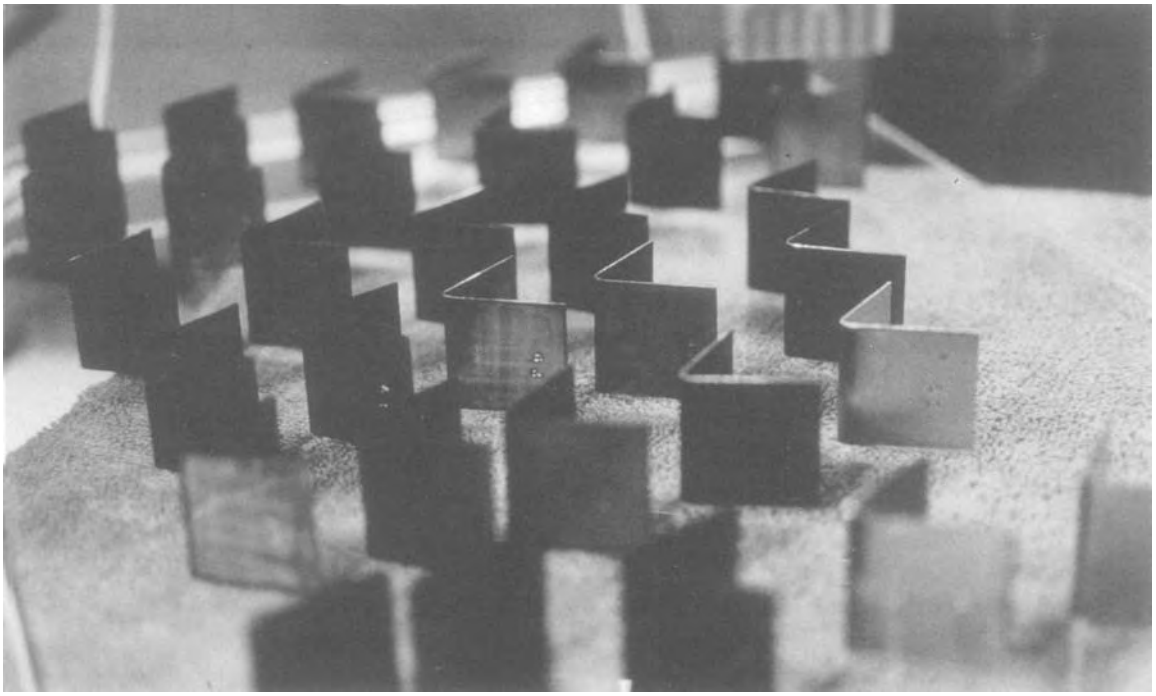

Figure 7. Bent coupons after Experiment 1, with large differences in tarnish levels.

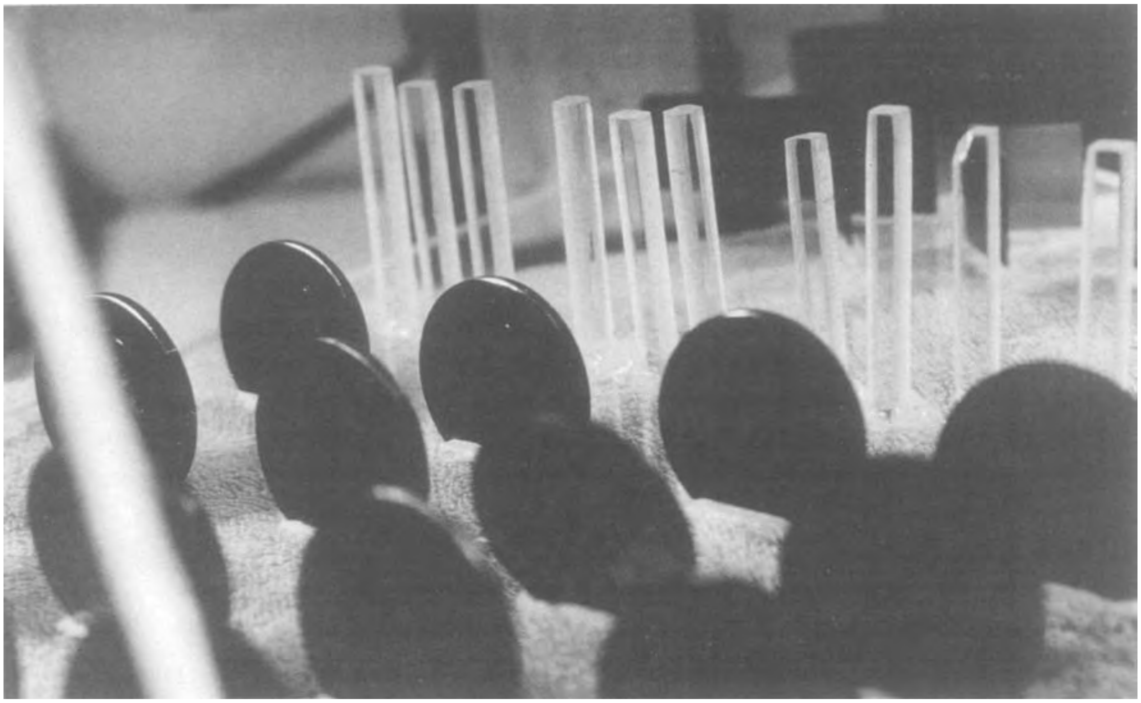

Figure 8. Overall darkening of silver coins after exposure to hydrogen sulfide. Coated glass tubes are also visible.